International Geology Review, Vol. 48, 2006, p. 1133–1144.

Strong Metal Anomalies in Stream Sediments from Semiarid Watersheds in Northern Chile: When Geological and Structural Analyses Contribute to Understanding Environmental Disturbances

ROBERTO OYARZUN[1]

Departamento de Cristalografía y Mineralogía, Facultad de Ciencias Geológicas, Universidad Complutense, 28040 Madrid, Spain

JAVIER LILLO,

Escuela Superior de Ciencias Experimentales y Tecnología, Universidad Rey Juan Carlos, Tulipán s/n, 28933 Móstoles (Madrid), Spain

JORGE OYARZÚN,

Departamento de Minas, Facultad de Ingeniería and CEAZA, Universidad de La Serena, Casilla 554, La Serena, Chile

PABLO HIGUERAS,

Departamento de Ingeniería Geológica y Minera, Escuela Universitaria Politécnica de Almadén, Universidad de Castilla-La Mancha, Plaza M. Meca 1, 13400 Almadén, Spain

AND HUGO MATURANA

Departamento de Minas, Facultad de Ingeniería, Universidad de La Serena, Casilla 554, La Serena, Chile

Abstract

We present data from a reconnaissance geochemical environmental survey (stream sediments) in the Limarí watershed (northern Chile), and include information from the neighboring Elqui Basin for a combined analysis. Given that the region has a long historical record of mining activities, important environmental disturbances were expected. However, one of the rivers in the Limarí watershed that was chosen to serve as a baseline, as no mining activities had ever taken place along the valley, showed one of the largest geochemical anomalies. The sampled stream sediments of the Hurtado River are highly enriched in Cu (50–1,880 $\mu g\ g^{-1}$), Zn (65–6,580 $\mu g\ g^{-1}$), and Cd (130–31,350 ng g^{-1}). The river system is sourced in the high-altitude domain of the Andes, and drains important Miocene hydrothermal alteration zones. The Coipita zone (El Indio gold belt) appears to be the most likely candidate to have originated the metal anomaly. The study of Landsat images suggests that the belt of alteration zones is located within a large (400+ km long, ~150 km wide) NW-SE dextral fault zone. This highly fractured domain may have conditioned the rapid unroofing of epithermal ore deposits in Miocene time, contributed to important circulation of meteoric waters, and eventually, to subsequent strong oxidation, leaching, and dispersion of metals, thus contributing to major metal dispersion in the Elqui and Limarí fluvial systems.

Introduction

THE LATE 1980S–1990S marked a major change in the emphasis and aims of geochemical surveys. While previously (1960s–1970s) the surveys were aimed at the detection of ore deposits, at present the characterization of metal environmental disturbances is becoming the centerpiece of many of these studies. However, the study of metal anomalies is much more than sampling, analyzing sediments or waters, and treating the data with sophisticated statistical tools. Metal dispersion is, above all, a geological process, and as such, it requires a careful analysis of the many factors (e.g., the geological, structural, and metallogenic settings, mineralogy, landscape, climate) controlling metal mobility. On top of this, we must add (if present) the type of mining (open pit, underground) and metallurgical (smelter, heap leaching, mineral dumps, tailings) operations taking place in the area under study.

[1]Corresponding author; email: oyarzun@geo.ucm.es

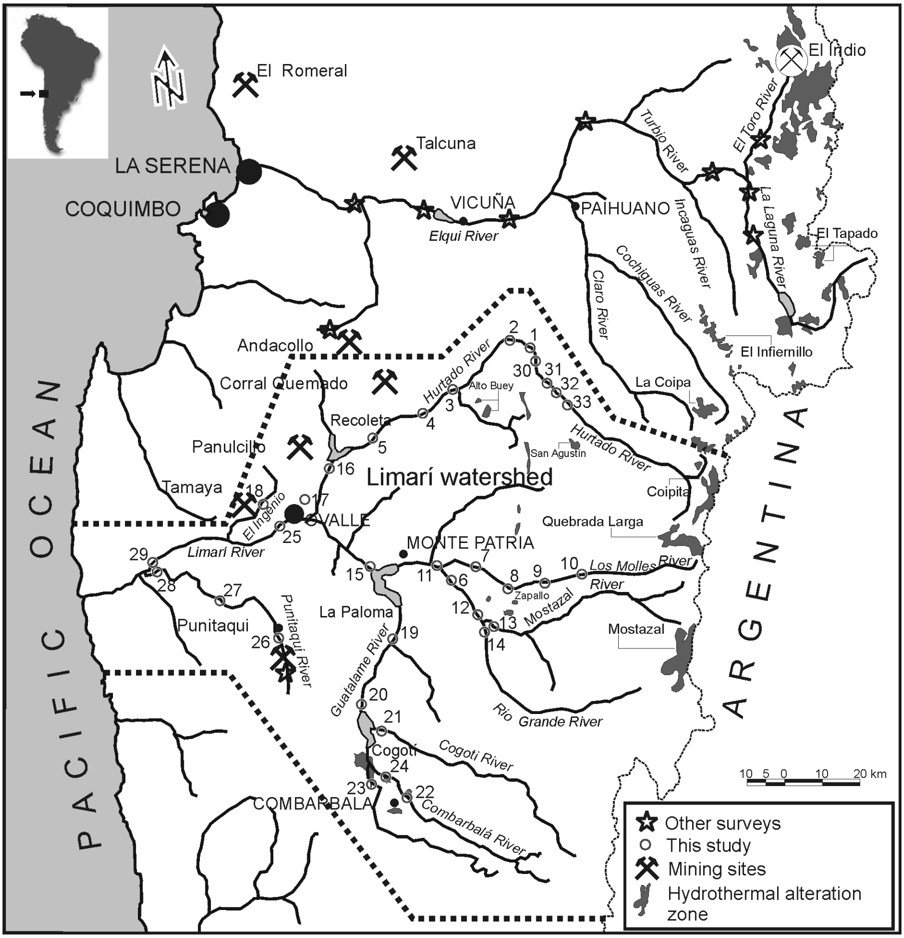

FIG. 1. The Coquimbo region, Limarí and Elqui watersheds, sampling sites, and location of mines and hydrothermal alteration zones. Hydrothermal zones are after Thomas (1967), Maksaev et al. (1984), and Kelm et al. (2001).

From 2002 to 2004 we carried out two geochemical surveys within the so-called *little north* (Norte Chico) of Chile, a semiarid transitional region (27°–33°S) located between the Mediterranean central part of the country and the Atacama Desert (deep north). This part of Chile is rich in mineral deposits and mining operations. Some of them are important in terms of historical significance, such as the Andacollo (Cu-Au) and Punitaqui (Cu-Au-Hg) mining districts (Fig. 1), which started operations during the Spanish colonial time (16th–18th century). Thus, the Coquimbo region (hosting the Limarí and Elqui basins) has a long record of mining-related environmental disturbances resulting from runoff and downstream dispersion of heavy metals (e.g., Higueras et al., 2004). However, metal dispersion in the region is also the result of long-lasting natural, geological processes related to the erosion of high-altitude (4000+ m above sea level) As-Cu-Zn–rich hydrothermal zones of Miocene age (e.g., Oyarzún et al., 2003; Oyarzun et al., 2004).

Except for a discontinuous coastal narrow belt, this semiarid realm is dominated by a complex array of valleys and rivers (the so-called *Valles Transversales* system) that flow in less than 150 km from the high Andean Mountains (>4000 m above sea level) to the coast. The main valleys are flanked by mountain belts about 50 km wide with altitudes of 600 to 1000 m above sea level. The climate is strongly conditioned by the Pacific anticyclone. The annual average temperature along the coast is 14°C, which increases towards the interior to 16°C. The average precipitation in the interior is 100 mm (e.g., Ovalle; average for the last 30 years), whereas that of the high-altitude Andean realm (rain + snow) is about 180 mm, with a minimum of 27 mm in 1981 and a maximum of 740 mm in 1987. However, the region is characterized by strong variations induced by westerly winds (Veit, 1996) that correlate with El Niño years, which bring intense rains and subsequent flash floods. A strong El Niño year usually has catastrophic consequences in this realm, such as those of 1997, when roads and bridges were cut by huge debris flows, moving sediments, and boulders, literally isolating the region from the rest of the country. We present here data for the Limarí watershed, and include geochemical information from the Elqui Basin (Oyarzun et al., 2004) (Fig. 1).

Methods

We took 33 samples of stream sediments (LIM samples) from the main rivers and streams of the Limarí watershed (Fig. 1; Table 2). The sediment samples (~2 kg) were collected from the rivers, focusing on the silty fraction, and stored in plastic bags. They were dried at room temperature and sieved to < 64 μm. The samples were digested in hot aqua regia (3:1 HCl: HNO_3), followed by dissolution with HCl (25%), which leaves behind a silica-only residue. The elements were analyzed by atomic absorption at Geoanalítica Ltda. (Chile) with the following detection limits: As (5 μg/g), Cd (20 ng/g), Cu (5 μg/g), and Zn (5 μg/g). Quality control at the laboratory is done by analyzing duplicate samples to check precision, whereas accuracy was obtained by using certified standards. Blank samples were also analyzed to check procedures. The mineralogy of the sediments was studied by XRD (instrument: Philips, model PW3040/00 X'Pert MPD/MRD) and SEM-EDX (instrument: Philips XL30; 25 kV) at the CAT facilities of Universidad Rey Juan Carlos (Madrid). In order to analyze the regional tendencies of element distribution, the results were treated with the Surfer 8 program, to assess the spatial continuity of data. For analytical procedures regarding data from the Elqui watershed, see Oyarzun et al. (2004).

Results

Mineralogy of stream sediments

The study of the mineral phase shows the presence of dominant quartz and plagioclase, plus secondary alteration minerals including kaolinite, illite, bramallite (Na illite), sericite, smectite, and vermiculite. The study also reveals the presence of gypsum, which is a relatively common mineral phase in the semiarid environment of northern Chile. The presence of kaolinite and smectite stresses the importance of alteration processes in the source area of some of the studied samples. For example, kaolinite and smectite are important in the higher course of the Hurtado River (e.g., samples LIM 2, 33), whereas near Ovalle (sample LIM 17; Fig. 1) the argillic mineral assemblage disappears. The metallic phase was studied by SEM-EDX. Given that the most important geochemical anomaly is located in the higher course of the Hurtado River, we concentrated our efforts in this sector. We found a complex array of intermediate mineral phases showing the effect of partial oxidation processes of sulfide grains. The compositions suggest the presence of pyrite, together with Mn and Fe oxides (Cu-Zn bearing), native copper, and ilmenite (e.g., sample LIM 2). Zinc was also detected in grains with a complex composition including Th-U or La-Ce-Pr-Nd-Sm-Gd, and P (e.g., sample LIM 31). This, together with the contents in Al and S in the grains suggests the presence of aluminum-phosphate-sulfate (APS)–like minerals, which are relatively common in the volcanic-epithermal environment (argillic alteration) and may accommodate REE, Th, and metals such as Fe, Cu, or Zn in their crystal structures (Dill, 2003).

The geochemical anomalies

Stream sediments sampling has proved to be an excellent geochemical tool in the tropical and arid and semiarid domains of the Andean chain, to detect the presence of ore deposits (e.g., Cruzat, 1984; Williams et al., 2000), to define baselines, and to constrain environmental disturbances (e.g., Williams et al., 2000; Higueras et al., 2004; Oyarzun et al., 2004). Compared to world baselines, the Limarí watershed sediments are highly enriched in Cu, Zn, As, and Cd (Tables 1 and 2), and the same applies to the Elqui Basin (Table 1). In order to have a better statistical approach to element distribution in the Limarí watershed, we transformed the data into log values. After mathematical treatment, most of the data displayed a normal (Gaussian) distribution of the bimodal type (Cu, Zn, and Cd) (Fig. 2). Arsenic departs from this behavior, with a flat distribution in the higher concentration range. The anomalous populations of Zn and Cd correspond to samples that were taken in the high course of the

TABLE 1. Mean Values for Cu, Zn, As, and Cd in Stream Sediments from the Limarí and Elqui Watersheds (Coquimbo Region), and World Baselines

Location	Cu µg g^{-1}	Zn µg g^{-1}	As µg g^{-1}	Cd ng g^{-1}	Reference
Limarí watershed					
All rivers	157	186	15	378	This work
Hurtado River	582	2117	52	9125	This work
Elqui watershed					
Elqui River	2352	470	202		Oyarzun et al., 2004
Elqui Holocene lacustrine sediments	697	3593	749		Oyarzun et al., 2004
Andacollo streams	417	161	7		Higueras et al., 2004
World averages (baselines)					
Stream sediments	39	132		1570	Callender, 2004
Stream sediments			5		Smedley and Kinniburgh, 2002
Pre-industrial baseline lacustrine sediment	34	97		300	Callender, 2004

Hurtado River, whereas in the case of copper, samples from the El Ingenio Stream (near the Panulcillo metallurgical plant; Ovalle) and Punitaqui (Cu-Au-Hg mining district) accompany the high Cu samples from the Hurtado River (Figs. 1 and 2). Given that no mining activities have ever been recorded along the Hurtado River, we must conclude that the Cu anomalous population has natural (Hurtado) and anthropogenic (Ingenio and Punitaqui) causes. The Hurtado River anomaly is extremely consistent, with very high concentrations of Cu, Zn, and Cd, displaying an almost perfect linear relationship between element pairs (Fig. 3).

In order to have a regional approach to element distribution, we added information for Cu, Zn, and As from earlier surveys in the Coquimbo region (Elqui watershed and mining districts) (Higueras et al., 2004; Oyarzun et al., 2004) (Fig. 1). Point linear interpolation for the Cu, Zn, Cd, and As data allows recognition of a major and consistent NW-SE regional trend (Fig. 4). Given that the sampling followed the rivers, and one of the fluvial trends is oriented NW-SE (Fig. 1), one may be tempted to interpret this direction as due to sampling bias. However, the rivers have a more complex pattern, and other fluvial directions are also important (Fig. 1). Thus, if the other directions are not reflected in the resulting 3D plots, then as discussed in the next section, this NW-SE trend may have further implications. The 3D plots show four well-defined element concentration highs (Fig. 4): (1) a conspicuous plateau-like zone for Cu, Zn, and As defined by geochemical data from the high course of the Elqui and Hurtado systems; (2) a single high for Cu, Zn, and As at the Ovalle-Panulcillo sector; (3) a single Cu high from Punitaqui; and (4) a minor high for Cu and As located at the Monte Patria zone. We discuss here the highs 2, 3, and 4, and offer an explanation for high 1 (Elqui and Hurtado) in the next section.

The Ovalle-Panulcillo and Punitaqui highs (2 and 3) (Figs. 1 and 4) can be explained in geological and industrial terms. The geology of the central part of the studied area (Thomas, 1967) is dominated by Cretaceous (Estratos del Reloj, Arqueros, Quebrada Marquesa, and Viñita formations) and Eocene (Los Elquinos Formation) volcanic and sedimentary rocks. These units were intruded by granitoids from Mid-Cretaceous to early Tertiary time, which gave rise to a series of mineral deposits (e.g., Punitaqui: Hg-Cu-Au; Tamaya: Cu) and hydrothermal alteration zones (e.g., Combarbalá) (Fig. 1). The Punitaqui district (Higueras et al., 2004) corresponds to

TABLE 2. Cu, Zn, Cd, and As Concentrations in Stream Sediments from Different Rivers of the Limarí Watershed[1]

Samples	Cu μg g^{-1}	Zn μg g^{-1}	Cd ng g^{-1}	As μg g^{-1}
Hurtado River				
LIM-1	864	3399	14893	48
LIM-2	730	2481	9582	14
LIM-3	153	598	2134	6
LIM-4	70	142	338	19
LIM-5	124	133	339	13
LIM-16	124	142	265	19
LIM-30	53	64	130	34
LIM-31	1131	4846	19970	114
LIM-32	686	2779	12250	69
LIM-33	1881	6586	31348	186
Los Molles, Grande, and Mostazal rivers				
LIM-6	76	97	139	12
LIM-7	46	83	180	10
LIM-8	47	134	378	13
LIM-9	59	216	660	13
LIM-10	27	163	280	3
LIM-11	51	92	100	6
LIM-12	76	149	492	20
LIM-13	138	135	297	5
LIM-14	80	97	237	14
LIM-15	103	91	278	16
Limarí River, El Ingenio Stream				
LIM-17	3082	308	756	23
LIM-18	202	45	<20	8
LIM-25	196	144	199	15
LIM-29	94	48	256	7
Guatulame River				
LIM-19	170	160	338	9
LIM-20	116	116	160	11
LIM-21	94	106	199	15
LIM-22	96	103	159	17
LIM-23	155	82	99	15
LIM-24	143	104	100	16
Punitaqui River				
LIM-26	491	42	219	9
LIM-27	228	51	<20	5
LIM-28	60	48	50	5

[1]See Figure 1 for location.

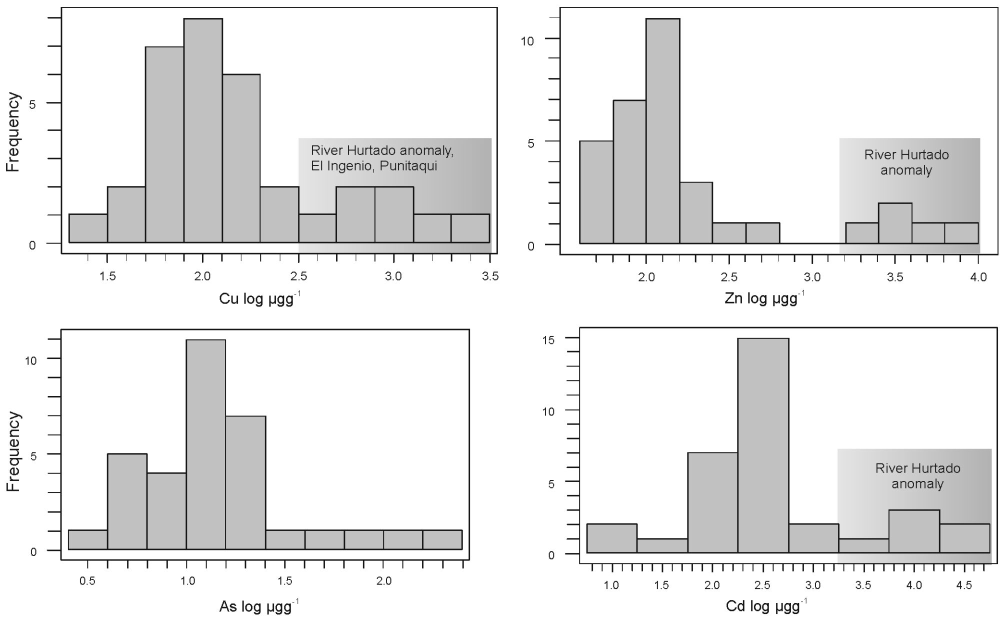

FIG. 2. Histograms showing log data distribution and anomalous chemical concentrations for the Limarí watershed.

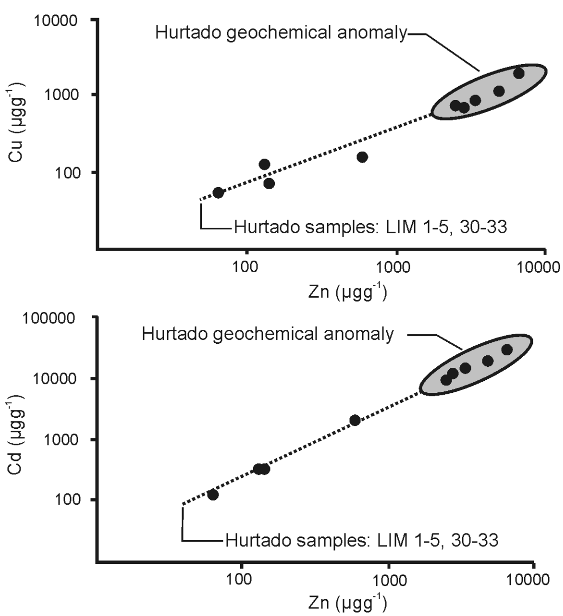

FIG. 3. Correlation plots for the Hurtado River data.

a complex case of shear-related, copper-gold and mercury mineralization. The copper-gold ore is located along the SSW-NNE Punitaqui shear zone, whereas the mercury ore is located within secondary fractures. The Cu-Au ore consists of the main minerals pyrite, tetrahedrite, native gold, chalcopyrite, and native copper, whereas the mercury mineralization consists of cinnabar. Only the Cu-Au ores are

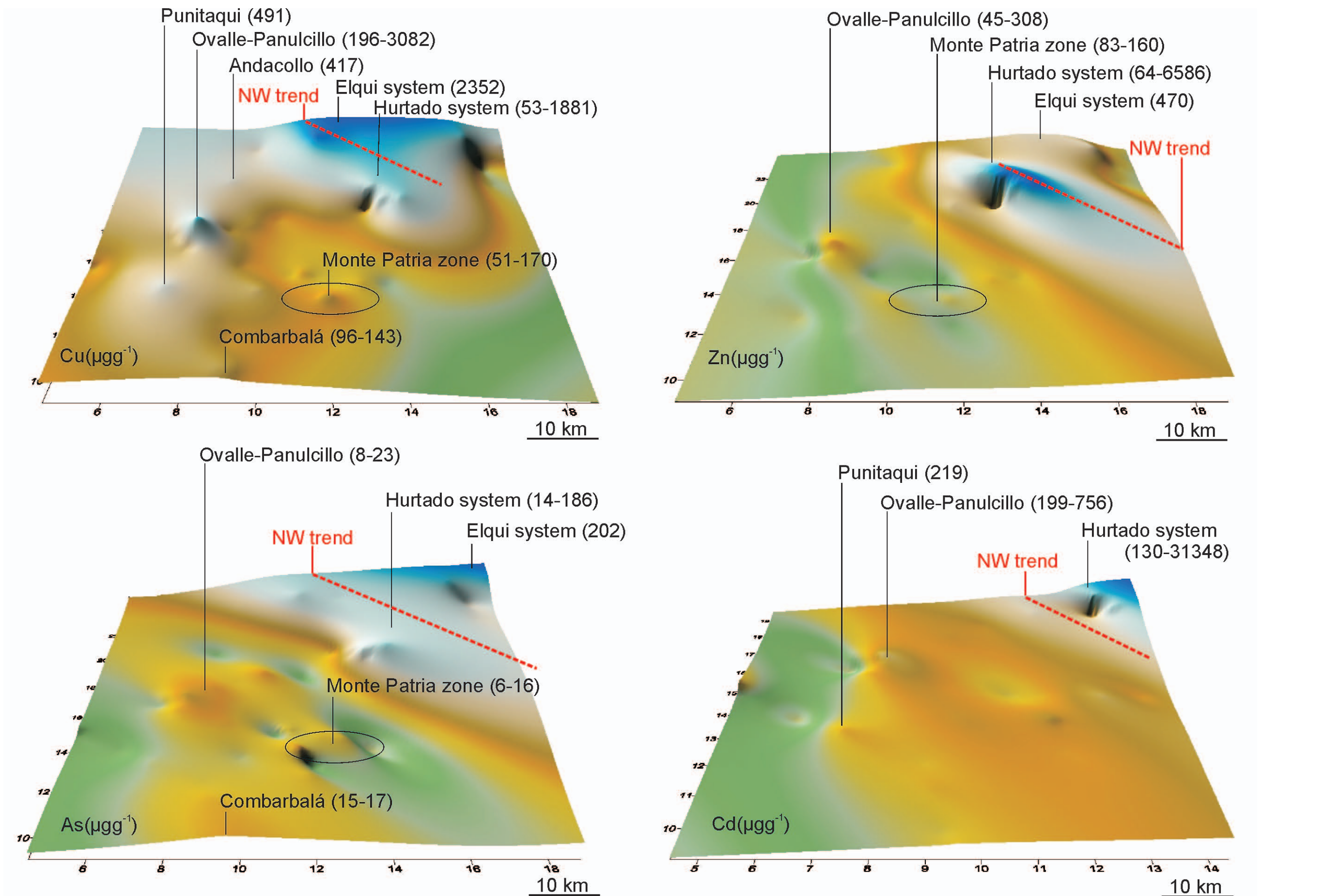

FIG. 4. 3D surface plots after point linear interpolation of data for Cu, Zn, and As from the Elqui and Limarí watersheds. Data for Cd: Limarí watershed only. Data between brackets: range (Limarí watershed) or average (Elqui watershed) concentrations.

presently mined in the district, and the major cause of environmental concerns in the sector is the removal of mineral dumps during stormy episodes (El Niño years), and the leaching of metals from the old leaching piles. (e.g., Higueras et al., 2004). On the other hand, Tamaya (main ore minerals: chalcopyrite, bornite) (Fig. 1), was a district of major importance during the second half of the 19th century, when it became the world's largest copper producer. However, the Ovalle-Tamaya high is also a consequence of other environmental hazards in the area. For example, the metal recovery plant of Panulcillo (a heap leaching operation adjacent to Ovalle) (Fig. 1) induces remarkable pollution along the El Ingenio Stream, with metal concentrations in sediments in the range of Cu: 155–29,500 μg g^{-1}, Zn: 70–3,600 μg g^{-1}, and Cd: 500–12,700 ng g^{-1} (Rojas, 2004).

The Monte Patria sector (high 4) (Figs. 1 and 4) lacks present or past mining/metallurgical activities; therefore the metal anomaly, although of lesser importance, may be related to the unique confluence of the rivers Mostazal and Los Molles, which drain an Andean sector hosting two large hydrothermal zones: Quebrada Larga and Mostazal. However, unlike the Coipita zone (Fig. 1), these appear to be of lesser importance in terms of metal dispersion. Other alteration zones in the central sector of the Limarí watershed include those of the Combarbalá sector (Cretaceous volcanic and volcaniclastic rocks) (Fig. 1). These Combarbalá alteration zones (e.g., Cogotí) are of the advanced argillic type, with strong silicification, although no epithermal mineralization has been recognized (Kelm et al., 2001). However, the silicified bodies contain copper minerals, and have anomalous As concentrations (Kelm et al., 2001), which may explain the relative highs for these elements detected in the 3D plots (Fig. 4).

Geological Interpretation of the Geochemical Anomalies: Discussion

Geological setting

The geology of the eastern, high-altitude sector of the region is dominated by Carboniferous granitoids (Elqui-Limarí batholith), Upper Paleozoic–Triassic sedimentary rocks, and a Middle to Upper Tertiary series of volcanic and intrusive units. Among the latter, two units are particularly relevant from the metallogenic point of view (Maksaev et al., 1984): the Doña Ana Formation (Upper Oligocene–Lower Miocene), with rhyolites, rhyolitic tuffs, andesites, and basaltic andesites, and the so-called Infiernillo Unit (Lower Miocene). The latter unit intrudes the Doña Ana Formation, and consists of small bodies of granite, granodiorite, monzodiorite, and diorite porphyries. These intrusions triggered widespread hydrothermal processes leading to formation of precious metal epithermal deposits (e.g., El Indio; Siddeley and Araneda, 1986) (Fig. 1). More than 30 large alteration zones with spectacular colors (red, green, yellow) can be defined within a N-S belt of ~200 × 20 km. Many of these zones comprise advanced argillic alteration mineral assemblages, with kaolinite, alunite, and jasper. The Miocene history of hydrothermal processes in this realm is long and complex (Bissig et al., 2002b), including barren events spanning from about 20–10 Ma, and a main episode of mineralization at 9.4–6.2 Ma. The barren period included both high- and low-sulfidation episodes, whereas mineralization was accompanied by mostly high sulfidation episodes. Bissig et al. (2002b) indicated that the high-sulfidation, pre-mineralization episodes in the main districts developed before incision of the pediment, whereas mineralization took place during formation of a major pediplain. Although the main hydrothermal episodes ended up by the Late Miocene, magmatic activity continued until the Late Pliocene (Bissig et al., 2002a).

Alteration zones present in the Andean sector of the Limarí watershed are those of Maksaev et al. (1984) (Fig. 1): (1) Coipita (27 km^2), granitoids and rhyolitic lavas intruded by the Infiernillo Unit (zone drained by the Hurtado River); (2) Quebrada Larga (26 km^2), granitoids and rhyolitic lavas intruded by the Infiernillo Unit (zone drained by the Hurtado and Los Molles rivers); and (3) Río Colorado (56 km^2), granitoids, rhyolitic lavas, and pelitic schists intruded by the Infiernillo Unit (zone drained by the Mostazal River).

Major lineaments: The regional structure

Lineaments may correspond to the superficial expression of ancient, deep crustal or trans-lithospheric structures (Richards; 2000). Salfity (1985) was one of the first to recognize the importance of major NW-SE and NE-SW lineaments in northern Chile–Argentina. These major structural trends are oblique to the main Andean direction (N-S) and their age is unknown. Richards (2000) relates the occurrence of porphyry copper deposits in northern Chile to the intersection of some of these lineaments with the West fissure zone. While inspecting a Land-

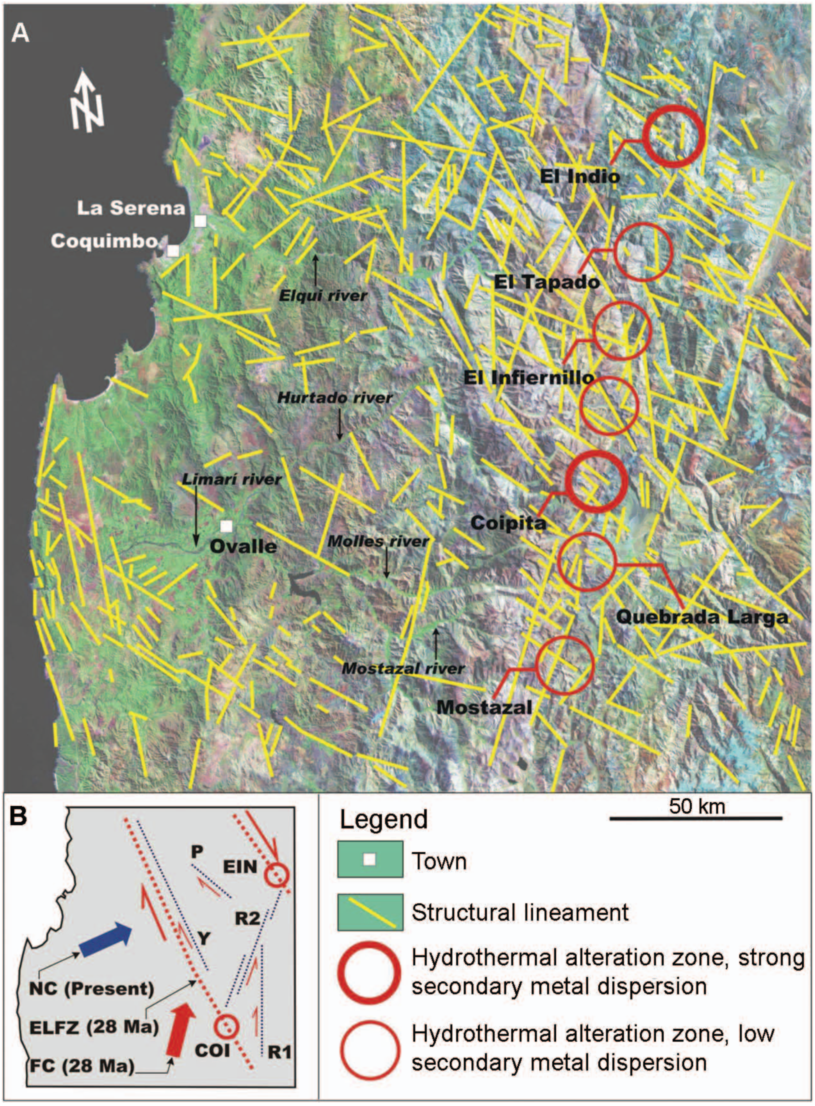

FIG. 5. A. LANDSAT 7 image including approximate location of main alteration zones, prospects, and epithermal ore deposits (red circles), and major structural lineaments (yellow lines). B. Structural interpretation of lineaments in terms of a NW-SE brittle fault zone. PYR-type structures after (*sensu*) Passchier and Trouw (1998). Abbreviations: COI = Coipita; EIN: El Indio; ELFZ = Elqui-Limarí fault zone; FC = Farallon plate convergence vector at ~28 Ma; NC = Present convergence vector for Nazca plate.

sat image of the region (LANDSAT 7 circa 2000; Orthorectified Landsat Enhanced Thematic Mapper Bands 7, 4, 2), we found striking evidence for a major zone of deformation trending NW-SE, with associated NNE-SSW and NE-SW structures, very much resembling fault development within shear zones (Fig. 5A). However, to generate a shear zone of this size and orientation, plate interactions must be strong and geometrically consistent. In other words, a roughly N-S oriented stress field would be required to generate a major fault zone of such a type and orientation. In this case the fault zone would be dextral and the NNE-SSW and NE-SW structures would represent R_1 and R_2 (Riedel 1 and

2) type structures (Fig. 5B). These, together with the inferred P and Y shears, constitute common shears found within brittle fault zones (Passchier and Trouw, 1998) (Fig. 5B).

The main objection to this idea comes from the present convergence between Nazca and South America, which is roughly ENE oriented (Fig. 5B). However, some clues for the understanding of the geodynamic setting of this realm can be found in the time span 28–20 Ma, a major turning point for the evolution of the Farallon–Nazca–South America system. Between chrons 10 (28.26 Ma) and 8 (25.81 Ma), the Chile ridge rotated from E-W to N40°W, a rotation that continued between chron 8 and chron 6 (20.16 Ma), from N40°W to N-S (Tebbens and Cande, 1997). It is during this time span that Farallon will be broken up into small plates including Nazca (in its southern realm), involving a change from extremely oblique (Farallon–South America) to almost perpendicular (Nazca–South America) convergence. In this respect, by Late Oligocene time subduction was fast and N to NNE directed (Cande and Leslie; 1986; Tebbens and Cande, 1997), which would have provided adequate geodynamic conditions to trigger major dextral NW-SE shearing at the regional scale (Fig. 5B). Thus, the inferred zone of deformation in the Coquimbo region could have been active by Oligocene time, and for the purposes of this work, we will name it the Elqui-Limarí Fault Zone (ELFZ). Given the clockwise rotation of the convergence vector of the Nazca-Farallon plate from Late Oligocene time onward (from NNE to ENE directed; Fig. 5B), movement along the ELFZ must have gradually stopped.

However, the sole presence of a structural domain at such a scale has enormous implications from the viewpoint of ore deposit formation and subsequent unroofing/secondary metal dispersion. As explained above, epithermal mineralization and formation of large zones of hydrothermal alteration took place by Middle Miocene time, in relation to the intrusion of the Infiernillo Unit (e.g., formation of El Indio). We suggest that the highly fractured crustal domain defined by the ELFZ may have facilitated the ascent of intrusive complexes, and as such, may have played at least a passive role in the formation of the gold belt. On the other hand, a highly fractured, positive domain would be more easily eroded, facilitating the infiltration of meteoric waters. Thus, erosion, oxidation, and metal leaching also may have been aided by the presence of the ELFZ.

Metal dispersion: evaluating secondary dispersion from alteration zones

Before we continue the discussion on the potential contribution of alteration zones to metal dispersion, two questions must be answered: (1) did all the alteration zones (regardless of their age and location) contribute to metal dispersion in equal terms? (2) If not, which zones (and why) contributed more to the process? Plutonic activity triggered the development of a N-S belt of alteration zones in the pre-Cordilleran sector (e.g., Alto Buey, Zapallo) (Fig. 1); the latter, however, are of minor importance (Thomas, 1967) and have no historical record of mining activities. Thus, in principle, we may rule out the role of these Cretaceous (?) alteration zones in the development of significant metal dispersion halos. For example, the stream sediments from the rivers Los Molles (LIM 7-10) and Mostazal (LIM 6, 12-14) (Zapallo alteration zone), show no important concentrations of Cu, Zn, As, or Cd (Fig. 1; Table 2). The same applies to the lower course of the Hurtado River (Alto Buey alteration zone) (samples LIM 3-5) (Fig. 1). On the other hand, not all the Miocene (Andean s.s.) alteration zones seem to have equally contributed to metal dispersion. For example, the Coipita and Quebrada Larga alteration zones are drained by tributaries of the Hurtado river; but the latter is also drained by the Los Molles River, and no important metallic contents are found in these samples (LIM 7-10) (Fig. 1; Table 2). The same applies to the Mostazal zone. Thus we are left with only one possibility—the Coipita alteration zone, which is now being evaluated intensively by a joint venture of mining companies.

At a larger scale, both the Coipita and El Indio alteration zones are located within the borders of the ELSZ, where R_2 type shears intersect the borders, and conspicuously, these are the only two alteration zones that generate strong metal dispersion in the Limarí and Elqui watersheds (see also Oyarzun et al., 2004 for the El Indio anomaly) (Figs. 5A and 5B). A complete analysis of this structural-geochemical setting goes far beyond the scope of this work; however, we believe that this intriguing relationship should be put forward and further investigated in future research on the area.

Lessons to be learned from the Elqui watershed: Final considerations

The Elqui survey (Oyarzun et al., 2004) provided some useful insights into the problem of evaluating the actual risk derived from mining operations.

Given the nature of the mining works in the El Indio-Tambo district (Fig. 1), it was relatively easy at first sight to find a clear culprit regarding the ultimate source of As contamination in the basin. However, a single sample taken away from the main river changed many things in our initial approach. The eventually fully sampled unit is a sequence of Lower Holocene lacustrine sediments (9640 ± 40 yrs BP, AMS radiocarbon date, Beta Analytic 175328; sample: HLS-17), which occur as perched outcrops on the mountain slopes, flanking the Turbio River for about 3 km (Fig. 1). This +10 m thick, As-rich sequence (up to 2344 mg g^{-1} As) comprises varved, alternating light-colored clay-gypsum beds and dark carbon- and gypsum-rich horizons, representing seasonal drier and wetter episodes. This unit represents the remnants of a small Early Holocene lake that most probably formed in response to extremely humid periods, associated landslides, and subsequent damming of the paleoriver system, a rather common process recorded in other sectors of the Andean realm (Trauth et al., 2000).

We must take into account that once erosion starts, the unroofing of a mineral deposit (a process enhanced in the high-altitude environment) may lead to the massive and sustained leaching of metals, and therefore, to long-lived "natural contamination" of rivers. The longer the process, the greater the effect, particulary if we are dealing with a highly fractured geological substrate (e.g., as within the ELFZ). As shown by the arsenic contents of the Lower Holocene sequence, we believe that the Elqui watershed proves this rule to be true. Does this mean that the mining operations at El Indio–Tambo have nothing to do with the arsenic contamination in the Elqui watershed? Hardly. It would be unreasonable to think that preparation of the mining areas (involving substantial road construction) and the development of open pit mining and metallurgical operations did not contribute with some arsenic to the river system.

All this brings us back to the Hurtado River issue. If, after evaluation, the Coipita prospect becomes an economic ore deposit, and mining operations begin, the environmental hazards along the Hurtado River will most probably increase. Given that the Hurtado River sediments already have extremely high concentrations of Cu, Zn, As, and Cd, well above world baselines (Table 1), the initiation of mining works at Coipita could increase the problem. If this has proved to be true in the Elqui system, there are no reasons to discard equivalent environmental disturbances along a river that mimics in many ways the high-altitude Elqui system.

Conclusions

The results of this work show that the region is being subjected to both industrial and natural contamination of Cu, Zn, As, and Cd (Figs. 2–4; Tables 1–2). The industrial hazards in the Limarí Basin are restricted to mining and metallurgical activities. In this respect, two contamination hotspots have been detected—the Punitaqui district and the Panulcillo metallurgical plant (Figs. 1 and 4), both inducing strong contamination. The largest geochemical anomaly is, however, of natural origin (high course of Hurtado River), and most probably related to the Coipita Miocene alteration zone, in the Andean domain of the watershed (Figs. 2–4). On the other hand, as shown by previous studies (Oyarzun et al., 2004), the El Indio mine (Au-Cu-As) (Fig. 1) is the other important contamination hotspot in the region. At a larger scale the elements show a consistent NW-SE regional trend (Fig. 4), which may be controlled by a large (inactive) fault zone (ELFZ) (Fig. 5). We suggest that the ELFZ may have played two key roles regarding ore deposit formation and subsequent erosion/metal dispersion. On the one hand, it may have facilitated (highly fractured realm) the emplacement of the Infiernillo Unit, which in turn triggered widespread hydrothermal activity, leading in specific cases to formation of epithermal precious and base metals deposits (e.g., El Indio). On the other hand, a highly fractured domain such as the ELSZ may have facilitated erosion, circulation of meteoric waters, and oxidation/leaching of metals. Both the Coipita and El Indio are located within the borders of the ELFZ (Figs. 5A and 5B) and, conspicuously, these are the most important zones in terms of metal dispersion.

Acknowledgments

This research was funded by Grant PPQ2003-01902 (Spanish Ministry of Education and Science). The field study was supported by the Research Office (Dirección de Investigación) of the University of La Serena (Chile).

REFERENCES

Bissig, T., Clark, A. H., and Lee, J. K. W., 2002a, Cerro del Vidrio rhyolitic dome: Evidence for Late Pliocene volcanism in the central Andean flat-slab region, Lama-Veladero district, 29º20'S, San Juan province, Argentina: Journal of South American Earth Sciences, v. 15, 571–576.

Bissig, T., Clark, A. H., Lee, J. K. W., and Hodgson, C. J., 2002b, Miocene landscape evolution and geomorphologic controls on epithermal processes in the El Indio–Pascua Au-Ag-Cu belt, Chile and Argentina: Economic Geology v. 97, p. 971–996.

Callender, E., 2004, Heavy metals in the environment—historical trends, *in* Lollar, B. S., ed., Treatise on Geochemistry 9, Environmental Geochemistry. Amsterdam, The Netherlands, Elsevier-Pergamon, p. 67–105.

Cruzat, A., 1984, Prospección geoquímica aplicada a yacimientos de oro: Revista Geológica de Chile, v. 21, p. 53–75.

Cande, S. C., and Leslie, R. B., 1986, Late Cenozoic tectonics of the southern Chile trench: Journal of Geophysical Research, v. 91, p. 471–496.

Dill, H. G., 2003, A comparative study of APS minerals of the Pacific rim fold belts with special reference to South American argillaceous deposits: Journal of South American Earth Sciences, v. 16, p. 301–320.

Higueras, P., Oyarzun, R., Oyarzún, J., Maturana, H., Lillo, J., and Morata, D., 2004, Environmental assessment of copper-gold-mercury mining in the Andacollo and Punitaqui districts, northern Chile: Applied Geochemistry, v. 19, p. 1855–1864.

Kelm, U., Pincheira, M., Oyarzún, J., and Sucha, V., 2001, Combarbalá advanced alteration zone, Chile: Geology, geochemistry, mineralogy and mineralization potential: Transactions of the Institution of Mining and Metallurgy, v. 110, p. 91–102.

Maksaev, V., Moscoso, R., Mpodozis, C., and Nasi, C., 1984, Las unidades volcánicas y plutónicas del Cenozoico Superior en la alta cordillera del Norte Chico (29º–31ºS): Geología, alteración hidrotermal y mineralización: Revista Geológica de Chile v. 21, p. 11–51.

Oyarzun, R., Lillo, J., Higueras, P., Oyarzún, J., and Maturana, H., 2004, Strong arsenic enrichment in sediments from the Elqui watershed, Northern Chile: Industrial (gold mining at El Indio–Tambo district) vs. geologic process: Journal of Geochemical Exploration, v. 84, p. 53–64.

Oyarzún, J., Maturana, H., Paulo, A., and Pasieczna, A., 2003, Heavy metals in stream sediments from the Coquimbo region (Chile): Effects of sustained mining and natural processes in a semi-arid Andean basin: Mine Water and the Environment, v. 22, p. 155–161.

Passchier, C. W., and Trouw, R. A. J., 1998, Microtectonics: Berlin, Germany, Springer, 289 p.

Richards, J. P., 2000, Lineaments revisited: SEG Newsletter, v. 42, p. 13–20.

Rojas, A., 2004, Contenido en metales pesados en sedimentos del estero El Ingenio, en un tramo de 6 km aguas abajo de la planta Ovalle de la compañía minera Panulcillo S.A., Región de Coquimbo: Unpubl. B.Sc. thesis, Universidad de La Serena, Chile, 134 p.

Salfitty, J. A., 1985, Lineamientos transversales al rumbo andino en el noroeste argentino: 4th Chilean Geologic Congress, Concepción, Chile, University of Concepción Press, v. 2, p. 119–137.

Siddeley, G., and Araneda, R., 1986, The El Indio–Tambo gold deposits, *in* Macdonald, A. J., ed., Gold '86, International Symposium on the Geology of Gold: Amsterdam, The Netherlands, Balkema, p. 3–22.

Smedley, P. L., and Kinniburgh, D. G., 2002, A review of the source, behaviour, and distribution of arsenic in natural waters: Applied Geochemistry, v. 17, p. 517–568.

Tebbens, S. F., and Cande, S. C., 1997, Southeast Pacific tectonic evolution from early Oligocene to present: Journal of Geophysical Research, v. 102, p. 12,061–12,084.

Thomas, H., 1967, Geología de la Hoja de Ovalle: Santiago, Chile, Instituto de Investigaciones Geológicas, 56 p.

Trauth, M. H., Alonso, R. A., Haselton, K. R., Hermanns, R. L., and Strecker, M. R., 2000, Climate change and mass movement in the NW Argentine Andes: Earth and Planetary Science Letters, v. 179, p. 243–256.

Veit, H., 1996, Southern westerlies during Holocene deduced from geomorphological and pedological studies in Norte Chico, northern Chile: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 123, p. 107–119.

Williams, T. M., Dunkley, P. N., Cruz, E., Acitimbay, V., Gaibor, A., López, E., Baez, N., and Aspden, J. A., 2000, Regional geochemical reconnaissance of the Cordillera Occidental of Ecuador: Economic and environmental applications: Applied Geochemistry, v. 15, p. 531–550.